How sensitive is tropospheric oxidation to anthropogenic emissions?

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[1] We use a global chemistry transport model to explore how changes in anthropogenic emissions alter ozone production and tropospheric oxidizing capacity over decadal (1990–2010) and centennial timescales (1900–2100). We find that the spatial extent of O_3 production and loss in the troposphere changes very little despite large projected increases in precursor emissions. While tropospheric OH shows a long-term decrease of only 20% between 1900 and 2100, there are widespread changes in distribution which alter regional oxidation capacity substantially. We show that the remote marine boundary layer remains an important net sink of O_3, as greater production related to increased continental NO_x emissions is outweighed by greater O_3 destruction. The critical NO_x level required to support net O_3 production doubles between 1900 and 2100, from 28 to 55 pptv on average, preventing any large-scale shift in production regime. **Citation:** Wild, O., and P. I. Palmer (2008), How sensitive is tropospheric oxidation to anthropogenic emissions?, *Geophys. Res. Lett.*, *35*, L22802, doi:10.1029/2008GL035718.

1. Introduction

[2] The lifetime of many pollutants in the global troposphere is governed by the abundance of the hydroxyl radical (OH). Photolysis of ozone (O_3) is the primary source of OH in the troposphere, and consequently the concentration and distribution of O_3 has important implications for the removal of these pollutants. Tropospheric O_3 is produced by the oxidation of CO, CH_4 and volatile organic compounds (VOCs) in the presence of nitrogen oxides (NO_x = NO + NO_2) and is lost by both chemical and physical processes with a lifetime of weeks to months [e.g., *Prather et al.*, 2001]. The balance between O_3 production (P) and loss (L) is determined by the relative abundance of NO_x and VOCs and varies with geographical location and season. The continental boundary layer is typically a net source of O_3 except in regions of intense NO emissions in wintertime. The marine boundary layer is generally a net O_3 sink, reflecting high humidity and a low abundance of NO_x [*Reeves et al.*, 2002; *DiNunno et al.*, 2003], although net production may occur in coastal regions influenced by continental pollutant outflow.

[3] Increasing anthropogenic emissions of NO_x, CO and VOCs have led to large increases in tropospheric O_3 over the past century [e.g., *Wang and Jacob*, 1998], and this trend is likely to continue [*Prather et al.*, 2003; *Stevenson et al.*, 2006]. This greater O_3 abundance alters the photochemical environment of the global troposphere by changing the supply of oxidants, and may alter patterns of O_3 production and loss. Previous model studies have focussed on changing radiative forcing or continental air quality but relatively few have explored changes in the oxidizing capacity of the troposphere [e.g., *Brasseur et al.*, 1998; *Lelieveld et al.*, 2002]. We focus here on changing oxidation and in particular on how photochemistry over clean oceanic regions, which we find to be responsible for almost 50% of chemical O_3 destruction in the global troposphere, may evolve as O_3 precursor emissions increase. Increases in marine background O_3 concentrations have been observed over eastern parts of the Pacific (0.3–0.8 ppbv yr^{-1}) [*Jaffe et al.*, 2003; *Parrish et al.*, 2004] and Atlantic (0.05–0.7 ppbv yr^{-1}) [*Lelieveld et al.*, 2004; *Derwent et al.*, 2007] oceans, and have been attributed to increased anthropogenic emissions of O_3 precursors. Recent analysis of ground-based and aircraft campaign data over the eastern mid-latitude Pacific between 1984 and 2002 suggests that the North Pacific is becoming less of an O_3 sink [*Parrish et al.*, 2004]. If the marine troposphere becomes less efficient in removing tropospheric oxidants, the effects of increasing anthropogenic emissions will be amplified, with potentially disastrous consequences for continental air quality.

2. Modelling O_3 Production

[4] We use the Frontier Research System for Global Change version of the University of California, Irvine (FRSGC/UCI) global 3-D chemistry-transport model (CTM) [*Wild and Prather*, 2000; *Wild et al.*, 2004] to examine the evolution of tropospheric photochemistry over decadal (1990–2000–2010) and centennial (1900–2000–2100) time scales. The CTM is run at T21 resolution (5.6° × 5.6°) with ECMWF meteorology for 1996. The five simulations described here use the same 1996 meteorology so that year-to-year variations in atmospheric transport do not influence the results. We discuss later how changes in meteorology and climate may affect our results.

[5] Emission data for 2000, 2010 and 2100 are based on the SRES A2p scenario [*Prather et al.*, 2001], and for 1900 are based on the EDGAR-HYDE dataset v1.3 [*van Aardenne et al.*, 2001] (Table 1). Emissions for 1990 are derived by applying a regional scaling to 2000 emissions based on changes in liquid fuel CO_2 usage for CO and VOCs and changes in total CO_2 usage for NO_x [*Marland et al.*, 2006]. Natural sources are held constant for 1990–2100, but soil and biomass burning sources, which are heavily influenced by human activities, are reduced for 1900 following EDGAR-HYDE. A uniform distribution of CH_4 was used in each scenario, with the abundance fixed at 900 ppbv in 1900 and 3730 ppbv in 2100 [*Prather et al.*, 2001]. Simulated present-day O_3 production and loss rates have been evaluated against observation-based rates derived with a photochemical

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Table 1. Trace Gas Emissions

	1900	1990	2000	2010	2100
		NO_x (Tg N/yr)			
Fossil fuel	2.0	31.6	31.8	38.9	109.0
Biomass burning	2.9	6.2	6.2	6.2	6.2
Lightning	5.0	5.0	5.0	5.0	5.0
Soil	2.9	5.6	5.6	5.6	5.6
Aircraft[a]	0.0	0.5	0.7	1.0	2.2
Stratosphere (NO_y)	0.5	0.5	0.5	0.5	0.5
Total	13.3	49.4	49.8	57.2	128.5
		CO (Tg CO/yr)			
Fossil fuel	96	649	650	750	2098
Biomass burning	229	496	496	496	496
Vegetation/ocean	200	200	200	200	200
Total	525	1345	1346	1445	2794
		VOC (Tg species/yr)			
Fossil fuel	17	201	201	214	402
Biomass burning	15	42	42	42	42
Isoprene	453	453	453	453	453
Total	485	696	696	709	897
		CH_4 (ppbv)			
Uniform distribution	900	1700	1760	1860	3730

[a]2050 projections used for 2100 scenario.

steady-state box model constrained by aircraft measurements (see auxiliary material[1]). The CTM reproduces these observation-based rates to within about 0.5 ppbv/day over marine regions, but underestimates boundary layer production close to East Asia, likely reflecting underestimation of O_3 precursor emissions [*Palmer et al.*, 2003] and limitations associated with model resolution. A more detailed analysis of the biases in simulating O_3 production is given by *Wild et al.* [2004].

3. Evolution of Tropospheric Oxidation

[6] Table 2 summarises changes in the photochemical environment of the troposphere between 1900 and 2100. The rates of O_3 production and loss increase by about a factor of three between 1900 and 2100, and the tropospheric O_3 burden doubles. Mean surface O_3 over the continents increases by 30 ppbv between 1900 and 2100; the 16 ppbv increase from 2000 to 2100 is comparable to that seen in previous multi-model studies using SRES A2 emission projections [*Prather et al.*, 2003]. Surface deposition is greatly increased, while influx from the stratosphere is marginally reduced due to a weaker cross-tropopause O_3 gradient. The net effect of these changes is that the troposphere shifts from being a net sink of O_3 of 40 Tg yr^{-1} to being a net source of 740 Tg yr^{-1}. The chemical lifetime of O_3 in the boundary layer is reduced by 25% from 12 days in 1900 to 9 days in 2100, and the mean global tropospheric lifetime drops by a similar amount, from 25 to 19 days.

[7] Figure 1 shows the global distribution of annual mean net O_3 production. Although NO_x emissions increase by an order of magnitude between 1900 and 2100, the regions of net production and loss remain remarkably constant, even though the magnitudes of production and destruction within each regime increase greatly. The transitions to net production in regions of continental or convective outflow are very limited in extent and are largely offset by reduced net production at high latitudes where the effect of shorter O_3 lifetime dominates. Net O_3 destruction occurs over 56% of the troposphere by mass, and this remains constant between 1900 and 2100 suggesting that changes in production and loss are well balanced and that the chemical regimes in the troposphere remain strongly buffered.

[8] The constancy of the distribution of O_3 production and loss regimes reflects the interaction of changes in chemical lifetime with atmospheric transport. The greater abundance of O_3 and its precursors in 2100 supports more active photochemistry in many parts of the troposphere, and in turn its shorter lifetime reflects an increased abundance of HO_2. While emissions of NO_x increase ten-fold from 1900, the tropospheric burden increases by only a factor of three as NO_x removal is greater; the mean tropospheric lifetime drops from 50 to 15 hours, limiting the extent of its redistribution from source regions. This lifetime reduction is driven by the increasing importance of NO_x self-reactions and PAN formation under high-emission conditions. Oxidation of CO, CH_4 and VOCs increases the abundance of peroxy radicals, but the relative increase in O_3 is larger and hence the efficiency of the NO_x catalytic cycle in producing O_3 decreases, from a global average of 0.30 to 0.21 molecules of O_3 per molecule of NO oxidized to NO_2. The number of times a nitrogen atom completes this cycle before oxidation to NO_y is also reduced, from 210 to 95, and consequently the ozone production efficiency (OPE, molecules O_3 produced per molecule NO_x oxidized) is reduced from 65 to 20 on a global basis. These effects are dominated by changes in the continental boundary layer; in the marine boundary layer and free troposphere the reduction in cycling efficiency is smaller (about 10%) and is balanced by increased cycling so that the OPE is relatively constant. Under low-NO_x conditions O_3 production is enhanced, but destruction of the higher background O_3 remains greater so that net production is reduced, see Figure 2. The critical NO_x abundance required to balance the production and loss of O_3 thus increases from 28 to 55 pptv between 1900 and 2100.

[9] How is this stability maintained? Tropospheric oxidation is strongly influenced by the OH radical, and gross production of OH increases by 70% between 1900 and 2000 and by a factor of 3 between 1900 and 2100. These results support and extend those of *Lelieveld et al.* [2002] who

Table 2. Global Tropospheric Trace Gas Budgets (Tg/yr)

	1900	1990	2000	2010	2100
O_3 Burden (Tg)	226	318	324	337	469
O_3 Chemistry	−37	292	299	348	736
gross production	2730	4760	4870	5200	8390
gross loss	2770	4470	4570	4850	7650
O_3 Deposition	479	795	801	847	1210
O_3 Stratospheric input	516	503	502	500	478
O_3 Lifetime (days)	25.4	22.1	22.0	21.6	19.3
CH_4 Chemistry	−311	−521	−543	−581	−1017
CH_4 Lifetime (yrs)	8.2	9.2	9.1	9.0	10.3
Mean surface O_3 (ppbv)	16.5	26.7	26.9	28.1	38.8
over continents	20.0	35.2	35.0	36.9	51.2
over open ocean	14.5	21.9	22.3	23.1	31.9

[1]Auxiliary materials are available in the HTML. doi:10.1029/2008GL035718.

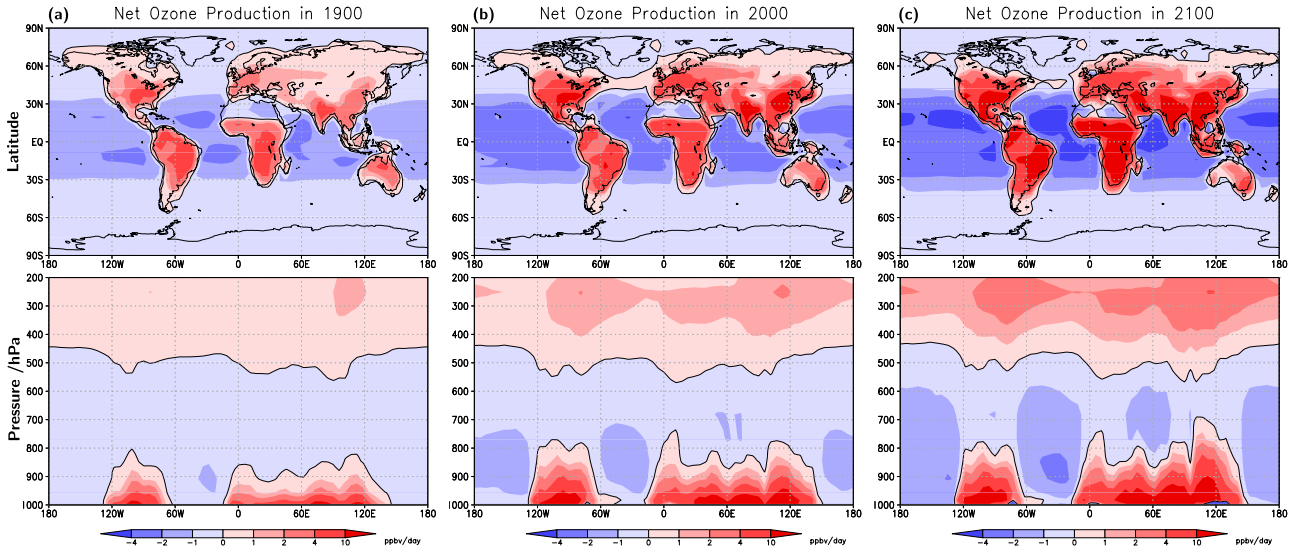

Figure 1. Annual mean distribution of net O_3 production in ppbv/day in (top) the boundary layer and (bottom) at northern mid-latitudes (20–60°N) in (a) 1900, (b) 2000, and (c) 2100. The contour line marks zero net production.

found a 60% increase since preindustrial times based on 1990 emissions. Primary production is greatest in the humid tropical marine boundary layer, but recycling of OH during oxidation of CO, CH_4 and VOCs provides a secondary source. In 1900, when reactive carbon levels are low, boundary layer OH is highest over the oceans, see Figure 3. However, much higher reactive carbon levels in 2100 lead to a greater increase in the sink of OH over the oceans than the source, and secondary formation over the continents is greatly enhanced. While global OH is reduced by 20% between 1900 and 2100, consistent with previous studies [e.g., *Prather et al.*, 2001; *Shindell et al.*, 2006] and causing an increase in CH_4 lifetime from 8.2 years to 10.3 years, there is a strong shift in OH abundance from oceanic to tropical continental regions. We find that the proportion of CH_4 oxidation occurring in net O_3 production regimes increases from 20 to 26%, indicating a shift in the location of peroxy radical production towards regions with higher NO_x. While long-lived greenhouse gases such as CH_4 are removed more slowly under 2100 conditions, we note that short-lived reactive VOCs and NO_x will be removed more quickly in polluted continental regions where the abundance of OH increases. However, short-lived trace gases of marine origin, such as dimethyl sulphide, will be removed more slowly under 2100 conditions.

[10] The decadal shifts in tropospheric oxidation are more subtle. Although changes in total emissions are small, there are significant shifts in the distribution of emissions equatorwards towards developing countries, and this leads to increased O_3 formation, as seen in previous studies [*Gupta et al.*, 1998]. We find a small decrease in CH_4 lifetime from 9.2 to 9.0 years between 1990 and 2010 associated with an increase in OH of about 0.1% yr^{-1}; this runs counter to the centennial trend and highlights the sensitivity of tropospheric oxidation to the location of emissions. *Wang et al.* [2004] found a similar trend in OH (+0.16% yr^{-1}) between 1988 and 1997 when neglecting changes in stratospheric O_3 column. Observation-derived trends show a decrease over this period [*Prinn et al.*, 2001] but may be strongly influenced by meteorological variability.

4. Implications for the Marine Troposphere

[11] Are the changes seen here consistent with long-term measurements over oceanic regions? We find that background O_3 increases by an average of 0.15 ppbv yr^{-1} between 2000 and 2010 over both the eastern Pacific and Atlantic Oceans, much less than the 0.35 ppbv yr^{-1} suggested by observations over the past decade [*Parrish et al.*, 2004; *Derwent et al.*, 2007]. O_3 destruction increases by 5% over much of the North Pacific, and we find no evidence to support suggestions that the efficiency of O_3 destruction may be decreasing in this region, or that the photochemical environment has changed substantially [*Parrish et al.*, 2004]. Gross O_3 production over the eastern Pacific is enhanced by 3–4% between 2000 and 2010 due to a similar increase in NO_x abundance maintained by a 6–8% increase in PAN. PAN decomposition makes an important contribu-

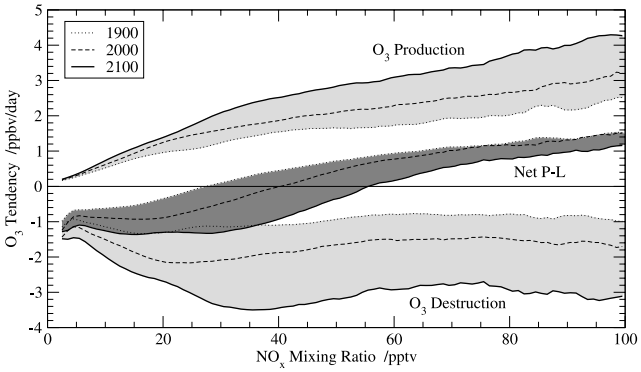

Figure 2. Tropospheric O_3 production and loss rates (ppbv/day) below 250 hPa (10 km) as a function of NO_x (pptv) for 1900, 2000, and 2100. The critical NO_x value for O_3 production occurs where net production (P-L) crosses zero, doubling between 1900 (28 pptv) and 2100 (55 pptv).

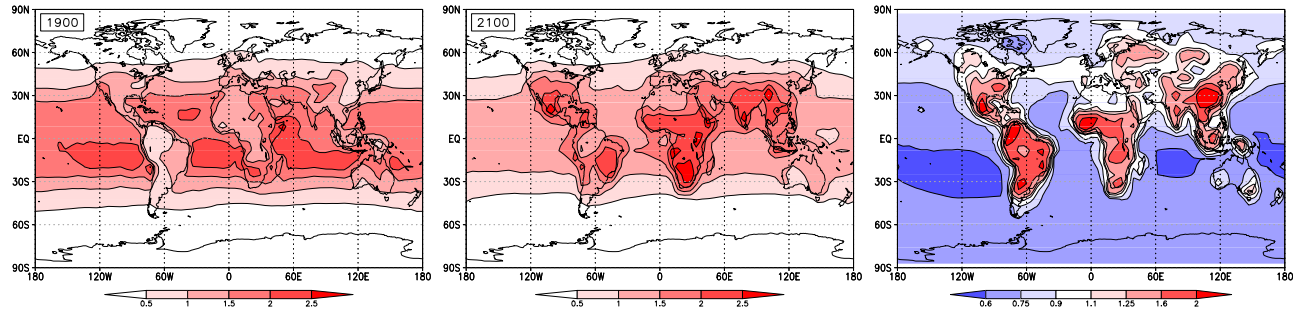

Figure 3. Annual mean distribution of OH (in units of 10^6 molecules cm^{-3}) in the boundary layer in (left) 1900 and (middle) 2100 and the relative change in OH given by (right) the ratio 2100/1900.

tion to O_3 production in this region [*Hudman et al.*, 2004], but we note that increases in PAN remain insufficient to prevent net O_3 destruction increasing even under the polluted 2100 conditions examined here.

[12] Although we find a clear shift towards increased net destruction on a monthly-mean basis, it remains possible that net production occurring during long-range transport of increasingly-polluted continental plumes over the oceans [e.g., *Auvray et al.*, 2007] may continue to increase. Future studies should examine the temporal variability in net production over this region, particularly during transport episodes in springtime. We also note that the present study does not account for recent rapid increases in shipping emissions which enhance O_3 in the marine boundary layer and are likely to reduce net O_3 destruction in coastal regions [*Eyring et al.*, 2007], and may thus contribute to explaining observed trends.

5. Concluding Remarks

[13] We have demonstrated that large projected increases in anthropogenic emissions between 1900 and 2100 have remarkably little effect on the geographical extent of net O_3 production and loss regimes, and thus that the 'remote' marine boundary layer remains a large net sink of anthropogenically-induced O_3. While we find a 20% reduction in global mean OH that indicates that the oxidation capacity of the troposphere is decreasing, redistribution of OH from marine to continental regions leads to substantial changes in regional photochemistry.

[14] In this exploratory study we have considered only a single scenario and have not explored the sensitivity of the results to the balance of NO_x and VOC emissions or CH_4. We have also neglected the influence of changes in climate so that we can isolate how tropospheric chemical regimes respond to increased emissions alone. Future increases in temperature and humidity are likely to enhance O_3 loss more than production, reducing the O_3 increases found here [*Stevenson et al.*, 2000], and will also enhance OH production, counteracting future reductions in tropospheric oxidizing capacity and moderating boundary layer OH redistribution. Projected changes in atmospheric circulation and stratospheric O_3 may lead to increased transport of O_3 from the stratosphere [*Collins et al.*, 2003; *Shindell et al.*, 2006], decreasing net O_3 production. More complex interactions, such as the influence of changes in temperature, CO_2 and O_3 on biogenic VOC emissions may also need to be considered. It would be valuable if future studies of tropospheric composition change diagnose the roles that these processes play in altering the balance of tropospheric photochemistry.

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